Heavy Metal Detection with Bismuth Film Electrode

Iain Laprade, Jen Olivero, and Gabby Servito
University of San Francisco, Department of Chemistry, San Francisco, CA 94117

Introduction

What are Heavy Metals?

Heavy metals are metallic elements that [1]:

- Have a high density and are toxic at low concentrations.
- Occur naturally in the Earth's crust and do not degrade over time.

At high concentrations they can cause adverse health effects:

- Zinc: Required for metabolic functions, high concentrations can result in pancreatic damage and arteriosclerosis.
- Lead: High concentrations can result in brain or kidney damage and reduced fertility [1].

Background

Over the course of this project, we used electroanalytical methods to determine the concentrations of heavy metals in water samples.

Square-Wave Stripping Voltammetry (SWSV)

Square-wave stripping voltammetry is a relatively inexpensive and easy-to-use method of electroanalysis [2].

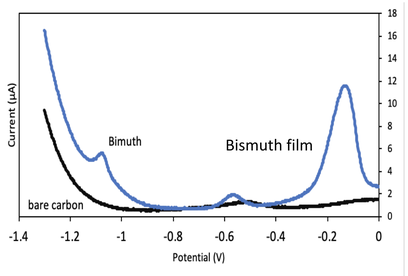
Cleaning
- An oxidizing potential is applied to remove any substance present on the electrode surface.

Accumulation
- Tested metal is applied to an electrode as a thin film via bulk electrolysis.
- A more positive potential is applied in order to strip the tested metal off the electrode through oxidation.

Detection
- Current is measured against potential to create a voltammogram.

Bismuth Film Electrodes (BFEs)

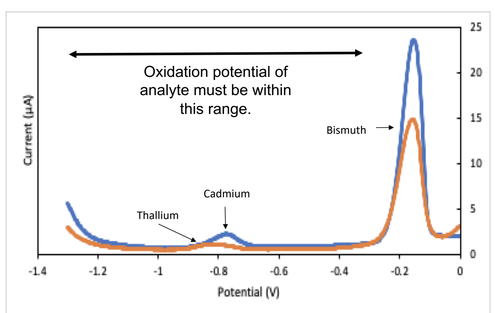
- In previous years, mercury was the norm for SWSV through the application of mercury film electrodes (MFEs).
- Bismuth film electrodes (BFEs) have served as an alternative to MFEs due to their comparable potential window and lesser environmental impact [3].



- Comparison of bare carbon electrode and bismuth-coated electrode.
- Bare carbon electrodes are unable to show peaks for the heavy metals tested in this work.

Heavy Metal Detection Using BFEs

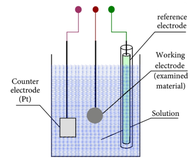
- BFEs have seen success in the detection of heavy metals with more negative oxidation potentials than bismuth [3].
- The oxidation of Bismuth occurs at around -200 mV vs. Ag/AgCl (1 M KCl).



Methods

0. Bismuth Electrode

- Bismuth was plated *in situ*.
- Glassy Carbon working electrode, platinum counter electrode, and a AgCl sat. electrode were used after initial testing using screen-printed carbon electrodes (SPCEs)



1. Creation of Standard Solutions

- Lead stock solution was created by measuring lead (II) chloride to create a 1000 ppm solution then diluted to 10 ppm
- Zinc, cadmium, and thallium solutions were prepared from an AA standard of 1000 ppm and diluted to 10 ppm with 0.1 M acetate buffer.
- A concentrated pH 4.5 buffer was made from sodium acetate and acetic acid and then diluted to 0.1 M.

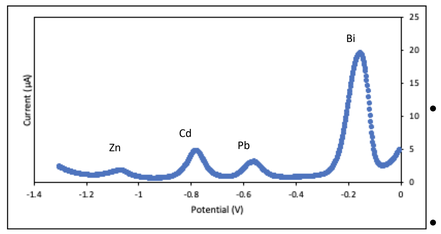
2. Calculation of Heavy Metal Concentration

- Peak currents from the standard addition of tap water were plotted on linear graph. Concentration of heavy metals were found by calculating for the x-intercept.

3. Detection of Heavy Metals in Unknown

- Unknown water sample came from the heating loop of Fromm Hall.
- Unfiltered unknown water sample was diluted by 1:10 ratio and simultaneously tested for heavy metals.
- Unknown water was filtered and diluted by the same ratio to be simultaneously tested.

Heavy Metal Detection

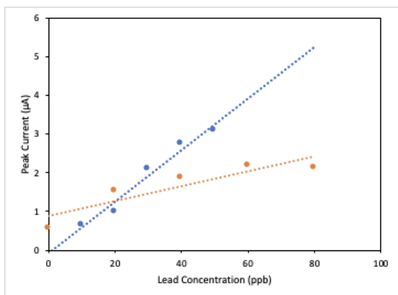


- Square wave voltammetry (SWV) was used to detect the peak current of the heavy metal present in solution.
- Calibration curves were created with deionized water to ensure linearity before standard addition in other solutions.
- Simultaneous testing allowed for the detection of multiple metals (lead, zinc, and cadmium).

Anodic Stripping Results

Comparisons Between SPCEs and Glassy Carbon Electrodes

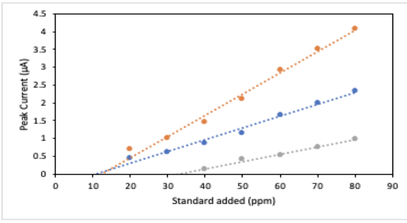
- Calibration curves for the detection of lead using screen-printed carbon electrodes (SPCEs) and glassy carbon electrodes.
- SPCE calibration curve (orange) exhibited far lesser sensitivity and linearity to glassy carbon data (blue).



Anodic SWSV Results

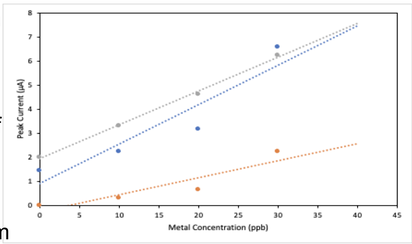
Determination of Heavy Metal Concentrations in Tap Water

- Simultaneous testing performed for Lo Schiavo tap water sample.
- Concentrations in tap water were too low as to provide accurate results using the prepared BFEs.
- Standard addition curves for cadmium (orange), lead (blue) and zinc (grey)



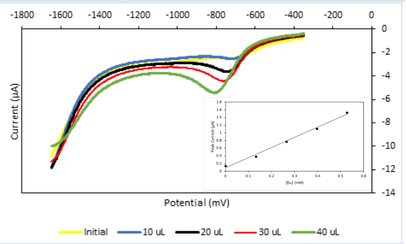
Determination of Heavy Metal Concentrations in Polluted Water

- Simultaneous testing performed for a 1:10 dilution of the Fromm Hall heating loop water sample.
- *In situ* bismuth plating and filtration allowed for simultaneous detection of cadmium, zinc, and lead.
- Standard addition plot for the filtered Fromm water sample.
- Standard addition curves for cadmium (orange), lead (blue) and zinc (grey)



Europium Detection Using BFEs

- *Ex Situ* bismuth plating was used for adsorptive stripping voltammetry in the detection of Eu through its complex formation with cupferron.
- Linear response observed with increased europium concentration.



Summary of Results

Table 1. Determination of Metal Concentrations by Standard Addition

	Deionized Water (Calibration)		Tap Water Sample		Fromm Water Sample (Filtered)		
Metal	LLOD (ppb)	LLOQ (ppb)	LLOD (ppb)	LLOQ (ppb)	LLOD (ppb)	LLOQ (ppb)	$[M^{2+}]$ (ppb)
lead (II)	3.55	11.27	13.48	19.97	11.68	38.928	32.3
cadmium (II)	6.80	25.00	13.11	15.67	10.1	33.683	--
zinc (II)	10.30	31.44	44.7	72.93	6	20.01	29.94

Note: US Environmental Protection Agency, Maximum Allowed Concentration in Drinking Water: lead (II) = 15 ppb and cadmium (II) = 5 ppb

Results and Outlook

- The simultaneous detection of the metals lead (II), cadmium (II), and zinc (II) was optimized using glassy carbon bismuth-film electrodes.
- Development of europium calibration curve indicates potential for improved detection with further optimization.
- Ultimately, the data shows the potential of using bismuth-plated glassy carbon electrodes for heavy metal detection.

Acknowledgments

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References

[1] Lenntech. Water Treatment Solutions: Heavy Metals. https://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm (Accessed Mar 15, 2019).
[2] Royal Society of Chemistry. Square-Wave Anodic Stripping Voltammetry. http://www.rsc.org/publishing/journals/prospect/ontology.asp?id=CMO:0000045&MSID=c2lc40063d (Accessed Mar 15, 2019)
[3] A. Economou. Bismuth-film Electrodes: Recent Developments and Potentialities for Electroanalysis. *Trends in Analytical Chemistry.* **2005,** 24, 4, 334-340.